

AMENDMENT(S) TO THE CLAIMS

This listing of claims will replace all prior versions and listings of claims in this application:

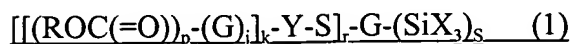
Listing of Claims:

1. (Currently amended) A method for increasing the hardness of silica/rubber mixtures comprising blending with said mixture at least one silane and a hardness-increasing amount of at least one member selected from the group consisting of thixotropic fumed silica[[:]], precipitated silica[[:]], an MQ resin wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$, and R^1 , R^2 , and R^3 R^a , R^b , and R^c are the same or different functional or non-functional organic groups[[:]], carbon black[[:]], a thermoplastic resin[[:]] and a thermosetting resin, wherein the silane is a blocked or unblocked mercaptosilane, and wherein the silica/rubber mixture optionally includes inorganic filler,

and wherein said hardness increasing amount is from 1 to 100 phr above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of bis-(triethoxysilylpropyl)disulfide) as the silane, and wherein the total amount of the member including any inorganic filler is above 100 phr and up to about 160 phr.

2. (Currently amended) The method of claim 1 wherein the silane is a blocked mercaptosilane ~~an organofunctional silane comprising at least one alkoxy group per silicon atom.~~

3. (Currently amended) The method of claim 2 wherein the ~~organofunctional moiety of the organofunctional silane is selected from the group consisting of mercapto, sulfide, disulfide, polysulfide, vinyl, acetylene, ureido, carboxyl, carbonyl, amino, epoxy, and halide~~ blocked mercaptosilane has a formula selected from the group consisting of:



and



wherein

Y is a polyvalent species (D)_zA'(=E), each wherein the atom (A') attached to the unsaturated heteroatom (E) is attached to the sulfur, which in turn is linked via a group G to the silicon atom;

each R is chosen independently from hydrogen, straight, cyclic, or branched alkyl that may or may not contain unsaturation, alkenyl groups, aryl groups, and aralkyl groups;

each G is independently a monovalent or polyvalent group derived by substitution of alkyl, alkenyl, aryl, or aralkyl wherein G can contain from 1 to 18 carbon atoms, with the proviso that G is not such that the silane would contain an α,β -unsaturated carbonyl including a carbon-carbon double bond next to the thiocarbonyl group, and if G is monovalent wherein $p = 0$, G can be a hydrogen atom;

X is independently a group selected from the group consisting of -Cl, -Br, RO-, RC(=O)O-, R₂C=NO-, R₂NO- or R₂N-, -R, -(OSiR₂)₁(OSiR₃) wherein each R is as above and at least one X is not -R;

D is oxygen, sulfur, or (-NR-);

A' is carbon, sulfur, phosphorus, or sulfonyl;

E is oxygen, sulfur, or NR;

p is 0 to 5; r is 1 to 3; z is 0 to 2; q is 0 to 6; a is 0 to 7; b is 1 to 3; j is 0 to 1, but it may be 0 only if p is 1; c is 1 to 6, preferably 1 to 4; t is 0 to 5; s is 1 to 3; k is 1 to 2, with the provisos that

(A) if A' is carbon, sulfur, or sulfonyl, then

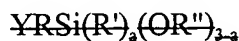
(i) $a + b = 2$ and

(ii) $k = 1$;

(B) if A' is phosphorus, then $a + b = 3$ unless both (i) $c > 1$ and (ii) $b = 1$, in which case $a = c + 1$; and

(C) if A' is phosphorus, then k is 2 .

4. (Currently amended) The method of claim 2 wherein the ~~organofunctional silane is defined by the formula:~~



wherein

~~R is a divalent alkylene, arylene, or aralkylene group of 1 to 20 carbon atoms, a vinyl group, or acetylenyl;~~

~~R' is a monovalent alkyl, aryl, or aralkyl group of 1 to 10 carbon atoms;~~

~~R" is a monovalent alkyl, aryl, or aralkyl group of 1 to 12 carbon atoms, wherein one or more of the carbon atoms can be replaced with a heteroatom;~~

~~Y is an organofunctional group selected from the group consisting of mercapto, sulfides, and polysulfides of the structure $R'''-S_x$, where R''' is a monovalent alkyl, aryl, or aralkyl group of 1 to 20 carbon atoms or the radical $-RSiR'^a_3(OR'')_a$, and x is 1 to 9, which resulting molecule must contain at least one alkoxy silane bond; other bis, tris, and higher silanes with sulfur or other heteroatom linkages in the groups between the alkoxy silane groups; vinyl; acetylenyl; carbonyl; amino; alkyl, aralkyl, or aryl substituted amino; ureido; thiocyanate; thiourea; epoxy; and hydrogen; and a is an integer and is 0, 1, or 2~~ rubber is selected from the group consisting of solution styrene-butadiene rubber, emulsion styrene-butadiene rubber, natural rubber, polybutadiene, ethylene-propylene co- and terpolymers, acrylonitrile-butadiene rubber, isoprene, polystyrene and poly α -methyl styrene, cis-1,4-polyisoprene rubber, styrene/butadiene copolymer rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis-1,4-polybutadiene, vinyl polybutadiene rubber, styrene/isoprene copolymers, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubbers containing 2 to 40 weight percent bound acrylonitrile in the terpolymer and combinations thereof.

Claim 5, (Cancelled).

6. (Original) The method of claim 1 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

7. (Original) The method of claim 1 wherein the silica/rubber mixture further comprises an inorganic filler.

8. (Currently amended) The method of claim 7 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc[,] and wollastonite. ~~alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite~~

9. (Original) The method of claim 1 wherein the member is thixotropic-(hydrophilic and hydrophobic) fumed (pyrogenic) silica.

Claims 10 to 13, (Cancelled).

14. (Original) The method of claim 9 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

15. (Original) The method of claim 9 wherein the silica/rubber mixture further comprises an inorganic filler.

16. (Currently amended) The method of claim 15 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc[[,]] and wollastonite, ~~alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite~~

17. (Original) The method of claim 1 wherein the member is precipitated silica.

Claims 18 to 21, (Cancelled).

22. (Original) The method of claim 17 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

23. (Original) The method of claim 17 wherein the silica/rubber mixture further comprises an inorganic filler.

24. (Currently amended) The method of claim 23 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc[[,]] and wollastonite, ~~alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite~~

25. (Currently amended) The method of claim 1 wherein the member is ~~an~~ the MQ resin.

Claims 26 to 29, (Cancelled).

30. (Original) The method of claim 25 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

31. (Original) The method of claim 25 wherein the silica/rubber mixture further comprises an inorganic filler.

32. (Currently amended) The method of claim 31 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc[[,]] and wollastonite. ~~alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite~~

33. (Original) The method of claim 1 wherein the member is carbon black.

34. (Original) The method of claim 33 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

35. (Original) The method of claim 1 wherein the member is a thermoplastic resin.

36. (Original) The method of claim 35 wherein the thermoplastic resin is selected from the group consisting of high-density polyethylene, ultra high molecular weight polyethylene, and low density-polyethylene.

37. (Original) The method of claim 35 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

38. (Original) The method of claim 1 wherein the member is a thermosetting resin.

39. (Currently amended) The method of claim 1 wherein the resin is a high glass transition thermoplastic resin.

40. (Original) The method of claim 39 wherein the high glass transition resin is selected from the group consisting of polyphenylene sulfide, polyamide, polyimide, polyamide-imide, polycarbonate, nylons, and polymethylmethacrylate.

41. (Original) The method of claim 39 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

42. (Currently amended) An article of manufacture comprising a silica/rubber mixture hardened by blending with said mixture at least one silane and a hardness-increasing amount of at least one member selected from the group consisting of thixotropic fumed silica $[[;]]_2$, precipitated silica $[[;]]_2$, an MQ resin wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$, and R^1, R^2 , and R^3 , R^a, R^b , and R^c are the same or different functional or non-functional organic groups $[[;]]_2$, carbon black $[[;]]_2$, a thermoplastic resin $[[;]]_2$ and a thermosetting resin, wherein the silane is a blocked mercaptosilane, wherein the silica/rubber mixture optionally includes inorganic filler, and wherein said hardness increasing amount is from 1 to 100 phr above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of bis-(triethoxysilylpropyldisulfide) as the silane, and wherein the total amount of the member including any inorganic filler is above 100 phr and up to about 160 phr.

43. (Original) The article of claim 42 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

44. (Currently amended) The article of claim 42 43 wherein said member is the MQ resin
~~article is a tire.~~

45. (Currently amended) The article of claim 43 44 wherein said article is a tire.